

Behavior of Phosphoric Acid in the Soil

A THESIS.

SUBMITTED TO THE UNIVERSITY FACULTY OF CORNELL
UNIVERSITY FOR THE DEGREE DOCTOR
OF PHILOSOPHY

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JAMES ADRIAN BIZZELL

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HISTORICAL

The fact that soils are capable of absorbing certain substances from solution has been known for nearly a century. There has been much discussion as to whom the credit for this discovery is due. The first authentic record appears to have been made by Gazzeri in 1819. He says: "If extract of dung strongly colored and containing nutritive matter is added to a clayey soil, the liquid is rapidly decolorized. The soil takes hold of the substances in solution, and forms with them compounds which are insoluble, but which are decomposed by the absorbing action of plants."

Bronner in his treatise on "Grape Culture in South Germany" published in 1836, made similar statements regarding the action of sand and garden soil, and Huxtable¹ in 1848, apparently ignorant of previous experiments, repeated the work of Gazzeri. A little later the work of these observers was extended somewhat by Thomson² of England.

In 1850 Way³ made a systematic investigation of the absorbing power of soils. His efforts were directed almost exclusively toward ascertaining the cause and nature of the absorption of bases. He published only one experiment on the absorption of phosphoric acid. When a solution containing calcium acid phosphate was filtered through a soil, no trace of phosphoric acid was found in the filtrate.

The next work bearing on the subject was that of Wicke⁴, who found that pure marble kept in contact with a solution of superphosphate evolved carbon dioxide, and the greater part of the phosphoric acid was precipitated.

Thenard⁵ was the first to make any systematic study of the absorption of phosphoric acid by soils. He succeeded in decolorizing the liquid from barnyard manure by the use of iron and aluminum hydroxides, and calcium carbonate. He concluded

¹ Jour. Roy. Agr. Soc., England.

² Ibid., 1850, **11**, 68.

³ Ibid., 1850, **11**, 313.

⁴ Ann. Chem. Phar., 1856, **99**, 97.

⁵ Compt. rend., **44**, 819.

that the active constituents of manure are removed in the soil by these compounds, and that the new compounds are decomposed slowly for the use of the plant. In a subsequent investigation¹, he always found phosphoric acid combined with aluminum and iron, and never with calcium and magnesium. He added solutions of calcium phosphate to the pure hydroxides of aluminum and iron, and to soil, and found after a few days that the filtered water contained calcium but no trace of phosphoric acid.

Deherain² examined a large number of soils. Some of these contained phosphoric acid insoluble in water charged with carbon dioxide, while others gave up phosphoric acid to this solvent. Soils containing compounds insoluble in carbon dioxide water gave up phosphoric acid to water containing calcium carbonate ammonium carbonate. A solution of calcium carbonate in water charged with carbon dioxide acted on iron phosphate producing calcium phosphate.

The role of phosphoric acid in the soil was taken up by Liebig³ in connection with his extended investigations on soil absorption. He determined the solvent effect of sodium chloride, sodium nitrate, and ammonium sulphate on phosphates of calcium and magnesium. In all cases appreciable quantities of the phosphates were dissolved. When the solutions thus made were added to soil the phosphoric acid was absorbed. Such changes were thought to have a favorable influence in bringing about the distribution of phosphoric acid in the soil.

Knop⁴ confirmed the observations of Thenard regarding the role of iron and aluminum hydroxides in soil absorption. He showed that phosphoric acid was fixed in greater amount and more rapidly when these compounds were added to soils, and that soils containing large quantities had greater reverting properties than those containing small amounts. Data were not accessible.

Peters⁵ endeavored to ascertain the state in which phosphoric acid is held in soils. He manured a soil with bone dust and

¹ Compt. rend., **46**, 212.

² Ibid., **47**, **47**, 988.

³ Am. Chem. Phar., **106**, 185.

⁴ Jahresbericht, 1865, 804.

⁵ Ann. Landw., 1867, 31.

treated the mixture with different solvents. From his results he concluded that phosphoric acid in soils is almost entirely combined with iron and aluminum, and that from a solution of calcium phosphate in carbon dioxide water, phosphoric acid is removed by soils only when then the latter contain hydroxides of iron and aluminum. Soils deprived of these compounds by treatment with acids are apparently indifferent to the phosphate solution.

In studying the fixing power of soils for phosphoric acid Voelcker¹ placed weighed quantities of six different kinds of loams in bottles, and added known quantities of superphosphate solution. He noted from time to time the amount of phosphoric acid still remaining in solution. The hydroxides present in the soils varied from zero to 17.38 per cent, and the carbonate of calcium from 0.15 per cent to 67.5 per cent. The phosphoric acid was fixed with especial ease by those soils which contained a good store of calcareous matter. The power of the clay soils to render the soluble phosphoric acid insoluble was far less than that of chalky soils.

Warrington² determined the effect of several substances on the solubility of freshly precipitated tri-calcium phosphate. He found that one per cent solutions of ammonium chloride increased the solubility in pure water, but that its addition to water saturated with carbon dioxide produced practically no effect. He observed also that when an excess of calcium carbonate was present, the amount of tri-calcium phosphate dissolved by carbon dioxide water was excessively small. The water became saturated with calcium carbonate, while only trace of the phosphate entered into solution. Even a very small amount of calcium carbonate was capable of producing this effect.

Two years later³ the same investigator carried out an elaborate experiment to show that the absorptive action of soil towards phosphoric acid is due to the formation of insoluble phosphates, by combination with hydroxides of iron and aluminum. Soils freed from lime were treated with solutions of calcium phosphate

¹ Jour. Roy. Agr. Soc., 1863, **24**, 46.

² Jour. Chem. Soc., 1866, **19**, 296.

³ Ibid., 1868, **21**, 1.

in carbon dioxide water. Almost all the phosphoric acid was retained by the soil, while the greater part of the calcium went into solution. The same results were obtained when hydroxides of iron and aluminum were used instead of soil.

Beyer and Biedermann¹ worked on the absorption of phosphoric acid by soils. Using a solution of sodium phosphate they found no definite relation between the amount absorbed and the quantities of iron, aluminum, and calcium contained in the soil, though there was increased absorption with increased quantities of these constituents. They determined the solvent action of solutions of calcium sulphate, sodium chloride, sodium nitrate, potassium chloride, and ammonium sulphate on the compound formed by absorption. No appreciable effect was observed.

Trochot² in his observations on volcanic soils noticed that fair amounts of lime and phosphoric acid were present, and that the fertility of these soils was very high in spite of their shallowness. The conclusion was drawn that the lime rendered the insoluble phosphates available.

The fact that the phosphoric acid of superphosphate gradually becomes insoluble in ammonium citrate solution was observed by Millott³, and Joulie⁴. Millot found the change to be due to the presence of large quantities of iron and aluminum oxides, while the results of Joulie seem to show that when an insufficient quantity of sulphuric acid to completely decompose the phosphate rock is used, (a condition which obtains in actual practice) the change is due to the formation of tri-calcium phosphate.

These experiments were extended somewhat by Albert and Vollbrecht⁵. They applied superphosphate to some soils containing large amounts of lime, and to others containing small amounts. With soils containing small quantities of lime, 6.5 per cent of the phosphoric acid of the superphosphate had become insoluble in ammonium citrate after eight days, while with those rich in lime, 15.4 per cent of the phosphoric acid had become

1 Chem. Centr., 1869, 945.

2 Compt. rend., 81, 1027.

3 Bied. Centr., 1875, 89—1879, 408.

4 Ann. Chim. Phys., Series 5, 1879, 244.

5 Bied. Centr., 1880, 84.

insoluble. These results were construed as proving the reversion of phosphoric acid by soils to insoluble phosphate of lime. In another experiment precipitated phosphates of iron and aluminum were added to soils with the result that none of the phosphoric acid became insoluble in ammonium citrate during eight days.

Petermann¹ attempted to determine the crop producing power of these various forms of phosphoric acid. The "citrate soluble" was in many cases superior to the "water soluble," though the results were not altogether satisfactory. The low value of the water soluble was due apparently to leaching, while the citrate soluble, being insoluble in water, was retained for the use of the plant.

Solubility determinations of the compounds supposed to exist in superphosphate were made by Albert and Wagner². Di-calcium phosphate was found to be soluble in water charged with carbon dioxide. Sulphates and chlorides appeared to have very little solvent action, while nitrates and carbonates were more effective. The solubility of precipitated phosphates of iron and aluminum in carbon dioxide water was a great deal less than that of precipitated calcium phosphate. Drying these salts lessened their solubility. Regarding the absorption of phosphoric acid by soils they found a solution of the phosphates in carbon dioxide water similar in its action to a solution of "soluble phosphoric acid." Absorption was most complete in clays poor in lime, less complete in calcareous clays and organic soils, and very small in sands poor in lime. An increase of humus in the soils rich in lime and clay was always accompanied by an increase in absorptive power.

In contradiction to the work just quoted, Fiedler³ states that solutions of nitrates dissolve less phosphoric acid from soils than pure water. His results showed absorption to be favored slightly by sodium nitrate. A solution of sodium nitrate did not affect the solubility of tri-calcium phosphate but it acted on di-calcium phosphate and phosphates of iron and aluminum.

¹ Bied. Centr., 1880, 87.

² Ibid., 1880, 640.

³ Landw. Versuchs-Stat., 26, 135.

Kostitcheff¹ working with pure compounds, obtained a decomposition of calcium carbonate in the presence of water and phosphates of iron and aluminum. Carbon dioxide was evolved and calcium phosphate was formed. The change took place even when there was present a large excess of iron with respect to the phosphoric acid.

Tuxen² investigated two soils—a sand and a clay—in order to ascertain the effect of chlorides of sodium and potassium, and sodium nitrate on the absorption of plant food. Phosphoric acid was readily taken up in the presence of the alkalies. Potassium chloride was the most effective, causing an increase in absorption of from 25 per cent to 40 per cent. Solutions of these salts were found to have little effect on the solubility of soil phosphoric acid.

Krocker and Grahl³ carried on manuring experiments with phosphates of various kinds. Oats and beets seemed to be little benefited by the soluble phosphates when used alone. When used in conjunction with ammonium sulphate there was decided increase in the crop, the greatest yield being obtained by the use of bone meal.

Similar experiments were made by Hoffmeister⁴. The various phosphates were applied as a top dressing. The results are interesting. In a sandy soil poor in lime the soluble phosphoric acid did not descend more than ten inches. Di-calcium phosphate remained unaltered during the experiment, and the mono-calcium phosphate was not converted into the tri-basic form.

Fleischer and Kissling⁵ studied the influence exerted by certain salts on the solubility of the phosphates present in peaty soils. Among the salts used were the sulphate, chloride, and carbonate of potassium, the sulphate and chloride of calcium, sodium nitrate, ammonium sulphate, and kainite. Potassium Sulphate was very effective, while sodium nitrate and kainite were far less so.

Gladding⁶ claims to have been the first to prove by direct

¹ Bull. Soc. Chim., (2) 1880, **34**, 341.

² Landw. Versuchs Stat., **27**, 107.

³ Bied. Centr., 1882, 1154.

⁴ Ibid., 1881, 813.

⁵ Ibid., 1883, 153.

⁶ Chem. News, **50**, 16, 27.

laboratory experiment, that the greater part of the phosphoric acid reverted in soils is in the form of iron and aluminum phosphates. On adding a solution of superphosphate to three representative soils he found after several days that all the phosphoric acid was soluble in ammonium citrate at a temperature of 65 degrees C. "This" the author states "shows that most of the phosphoric acid was present in the form of iron and aluminum phosphates, since tri-calcium phosphate is much less readily attacked by this reagent than these phosphates." The author criticizes results obtained by Albert and Vollbrecht¹, from which these investigators concluded that the phosphoric acid not dissolved by ammonium citrate at 40 degrees C had become insoluble tri-calcium phosphate. Unfortunately Gladding did not give the composition of the soils used in his experiments.

The composition and action of superphosphate have been studied from many points of view. Weilandt² found it to be very completely absorbed by marl. The action was rapid. Margestein³ showed its value to be increased by mixing with wood ashes. He grew potatoes, mustard, barley, and maize on a diluvial sandy soil. Quantities of ashes up to 25 per cent were beneficial. Analyses of soils used were not given.

From his results Joffre⁴ referred reversion to the formation of phosphate of iron. He determined its coefficient of solubility in water, in water charged with carbon dioxide, and in solutions of different salts. In all cases it was less sensitive to these substances than tri-calcium phosphate. Vegetation tests showed it to be less valuable.

Thompson⁵ determined the absorptive power of sand, as well as that of the same sand containing known quantities of orthoclase, calcium carbonate, iron and aluminum hydroxides, of mixtures of calcium carbonate and orthoclase, and of calcium carbonate and hydroxides of iron and aluminum. He also noticed the effect of sodium chloride and potassium nitrate on the process of absorption. The original publication was not

¹ Bied. Centr. 1880, 87.

² Landw. Versuchs-Stat., 34, 207.

³ Bied. Centr., 1888, 225.

⁴ Bull. Soc. Chim., 47, 312.

⁵ Inaug. Dissertation, Dorpat, 1890.

accessible but abstracts give the following conclusions. "Sand offers no resistance to the extraction of the phosphoric of superphosphate by water. Addition of orthoclase produces no effect. Calcium carbonate combines quickly with soluble phosphoric acid. Iron and aluminum hydroxides are also active in retaining phosphoric acid. The compounds formed with iron and aluminum are more stable towards salt solutions than tri-calcium phosphate. Sodium chloride solutions (1 per cent and 2 per cent) dissolve less phosphoric acid from superphosphate than pure water. In the presence of calcium carbonate and hydroxides of iron and aluminum the salt solutions dissolve more than pure water."

The action of carbon dioxide on tri-calcium phosphate alone and in the presence of ferric hydroxide was studied by Geogievic¹. Tri-calcium phosphate suspended in water was decomposed by carbon dioxide, but the reaction was far from being complete. When ferric hydroxide was also present decomposition took place, but the phosphoric acid immediately combined with the iron. Under some conditions the whole of the phosphoric acid was withdrawn from the calcium salt. These results confirm the observations of many previous workers, namely, that all of the phosphoric acid in calcium phosphate when applied to the soil finally becomes converted to phosphate of iron.

Some interesting facts regarding the assimilation of phosphoric acid by crops were obtained by Deherain² on the experimental plots at Grignon. He noticed that the sum of the phosphoric acid in drainage and crops in ten years, was not equal to the phosphoric acid not extracted by acetic acid. He concluded that the calcium phosphate was changed to iron and aluminum phosphates after a time. A soil was mixed with tri-calcium phosphate and placed in a seltzogene. After a few days no phosphoric acid was dissolved by water charged with carbon dioxide, although tri-calcium phosphate is soluble in this mixture. He does not state whether the soil contained lime. Ferric and aluminum phosphates were assimilated by oats but not by wheat.

¹ Monatsh., 1891, 12, 566.

² Ann. Agron., 17, 445.

Kellner¹ made some observations on the action of lime as a manure on paddy fields. Complete infertility had resulted in several places. He attributed part of this to loss by leaching. Among other things the action of phosphates in two soils was investigated. He mixed in from 0.25 per cent to 5 per cent of quicklime, and after two weeks added a solution of potassium trihydrogen phosphate. Lime apparently caused an increase in the soluble phosphoric acid. The maximum effect was obtained with 1 per cent to 2.5 lime. After two months still more phosphoric acid had become soluble.

Gerlach² repeated Thompson's work³ on the absorption of phosphoric acid by soils. The results here recorded show that clay, peat, and sand which have been extracted with hydrochloric acid have no power of absorbing free phosphoric acid, sodium phosphate, and superphosphate. Calcium and magnesium carbonates absorb phosphoric acid, while iron and aluminum oxides do so very completely. In the first case the compounds formed are comparatively soluble and are completely extracted by water charged with carbon dioxide. The compounds formed with iron and aluminum are insoluble in water even in the presence of carbon dioxide, but are more or less dissolved by the prolonged action of organic acids. He endeavored to determine the form in which phosphoric acid is absorbed. A solution of mono-calcium phosphate was placed in contact with calcium carbonate. Di- and tri-calcium phosphates were formed depending on the relative amounts of the materials used. When iron and aluminum hydroxides were the absorbents, not only was the phosphoric acid absorbed, but the calcium was also retained. Di-calcium phosphate and an iron phosphate were formed. The author concluded that normal ferric phosphate is formed when sufficient ferric hydroxide is present. A basic phosphate of iron was also considered a possibility.

Stocklasa⁴ estimated the yearly loss of calcium carbonate from various soils. The results are of interest as bearing on the

¹ Bull. Coll. Agr. Tokyo Imp. Univ., 1891, 9, 1.

² Landw. Versuchs-Stat., 1895, 46, 201.

³ Inaug. Dissertation, Dorpat., 1890.

⁴ Bied. Centr., 1895, 82.

loss of phosphoric acid. Four soils—loam, marl, clay and humus—were analysed and the total phosphoric acid compared with that found in the drainage water. From the data thus obtained the annual loss was estimated. The results showed a loss of 9146 grams per hectare in the case of the clay, while the humus lost 21995 grams per hectare. The humus contained the smallest per cent of phosphoric acid, but lost the largest amount.

Schreiber¹ grew oats followed by turnips on sandy, humus, and loamy soils using two fertilizers, viz: (1) a mixture of di-calcium phosphate, calcium sulphate, and magnesium carbonate, (2) a mixture of sodium phosphate, and carbonates of calcium and magnesium. The first mixture gave the best results in every case. The author thought that the diminished action in the second case was due to the precipitation of phosphoric acid by the carbonates of calcium and magnesium. His results with peaty soils showed that the humus phosphoric acid, soluble in alkaline ammonium citrate, was almost useless for vegetation. In some cases the humus acted on the assimilable phosphoric acid in a manner analagous to calcium carbonate.

Joffre² made vegetation experiments to determine the relative values of superphosphate, tri-calcium phosphate, and the ferric phosphate obtained from a sample of manure containing very little tri-calcium phosphate. Crops of mustard were grown on plots which differed only with regard to the nature of the phosphate present. The ferric phosphate was little better than no fertilizer, while the other phosphates gave a large increase.

On mixing basic slag and superphosphate with soil, Smorawski and Jacobson³ noticed that the phosphoric acid originally soluble in water was rapidly converted to the citrate soluble form, and this compound underwent no further change.

Stoklasa⁴ called attention to the fact that ferrous salts in the presence of phosphoric acid soluble in water, give rise to the production of di-tri-ferric phosphate, unless there is an excess of free phosphoric acid present. With soluble phosphoric acid

¹ Exp. Sta. Rec., 1895, 804.

² Bull. Soc. Chim., 1896, (3) 15, 42.

³ Bied. Centr., 1896, 580.

⁴ Ann. Agron., 1897, 23, 588.

aluminum salts do not form compounds analagous to those of ferrous and ferric salts, but behave like salts of calcium and magnesium. No data were given.

Prianischnikoff¹ working on the relative values of mineral phosphates, made sand culture experiments with cereals manured with phosphorites. The phosphoric acid was only slightly available. Under the same conditions certain other plants such as peas, lupines, buckwheat, and mustard seemed to be able to utilize the phosphoric acid. The "podzols" (soils containing a large amount of fine siliceous and organic matter) were apparently able to render phosphorites available for cereals and other plants. The same was true of forest and peaty soils. Some of the black soils, however, were without action on the phosphorites.

The results of numerous experiments conducted by Ullmann and Grimm² showed that for months after the application of superphosphate, phosphoric acid soluble in water passed through a depth of soil equal to ten inches. The authors found only a portion of the magnesia, lime, and oxides of iron and aluminum, available for retaining phosphoric acid. The mechanical fixation appeared to depend on the amount of fine sand present, especially sand of the fineness of dust.

A series of experiments, on the use of lime, extending over several years, have recently been carried out at the Rhode Island Experiment Station³. The practical results obtained in field tests by the use of lime in conjunction with phosphates are of particular interest, and apparently contradictory to a majority of the writers on agricultural chemistry. Because of its peculiar interest, the work is quoted here in some detail. Crops were grown for four successive years, and the average yields on the limed and the unlimed plots recorded. The results on the yields of hay are given herewith as being typical of those obtained with the crops grown. The figures represent pounds per acre.

¹ Ann. Agron., 1899, **25**, 177.

² Chem. Ind., 1900, **23**, 61.

³ R. I. Agr. Expt. Sta. Bull., No. 58.

Forms of Phosphoric Acid Applied.	Limed.	Unlimed.	Gain from Liming.
Dissolved Boneblack.....	19,837	9,820	10,016
Dissolved Bone.....	19,281	8,564	10,716
Dissolved Phosphate Rock.....	20,205	8,951	11,253
Fine Ground Bone.....	22,012	11,855	10,157
Basic Slag Meal.....	20,400	13,193	7,206
Floats.....	20,525	10,560	9,965
Alumina Phosphate (raw).....	14,387	5,042	9,345
Alumina Phosphate (ignited).....	19,481	4,930	14,551
No Phosphoric Acid.....	15,737	2,547	13,190
Double Superphosphate.....	17,937	4,752	13,184

It will be seen that there was a wonderful gain in the crop, in all cases, resulting from the use of lime. The acidulated phosphates appeared to be helped more by the lime than the unacidulated forms. The authors suggested that lime might have been beneficial by correcting the acidity of the first. No experiments, however, were made to ascertain whether the lime would liberate phosphoric acid from the insoluble phosphates of the soil.

Some rather peculiar results were obtained by Schreiber¹ on the action of calcium carbonate on mineral phosphates. Addition of calcium carbonate to the phosphates decreased the action of the latter on the crops grown, the greater the amount, the greater the injury. In some cases the effect extended to the next year. The action of basic slag was not affected.

Kellner and Bottcher² obtained similar results, when using superphosphate, basic slag, and bone meal for oats. Addition of calcium carbonate caused reduced yields in every case, but this decrease was less with the superphosphate and slag than with the bone meal. Comparing the amounts of increase due to phosphoric acid applied, the addition of calcium carbonate was not unfavorable when used in conjunction with slag and superphosphate. With bone meal the addition of calcium carbonate reduced the yields on the average by 67 per cent. No explanation was offered for the action of the latter.

The relation between humus and the phosphoric acid of the soil, has not received very much attention. Incidentally, obser-

¹ Bied. Centr., 1900, 162.

² Deut. Landw. Presse, 1900, 27, 665.

vations have been made on the retentive and solvent powers of some organic soils, but in most cases the work was designed for the investigation of other problems.

Fleischer and Kissling¹, in a study of the action of moorland soils on insoluble phosphates, found that the effect was to render a portion of the phosphate soluble in water, amounting in one case to 5.5 per cent of the total. At the same time a portion was reduced to the di-calcium salt, and in one compost as much as 17 per cent of the total was brought into this form. When the ratio of soil to phosphate was widened, there was an increase in soluble salt. This increase varied directly with the time of contact. There appeared to be a limit beyond which the soluble salt became reduced.

In 1892 Berthelot and Andre² made some experiments on the absorption of phosphoric acid by artificial humic anhydride prepared from sugar. Solutions of phosphates of sodium and ammonium were mixed with the acid anhydride and allowed to stand in the cold for twenty-four hours. The absorption from these salts were very small. In most cases practically no phosphoric acid was retained.

The action of humic acid in the soils on the solubility of various natural phosphates was taken up by Minssen and Tacke³. Many of the insoluble phosphates were acted on in the presence of the free humic acid of the soil. When lime was added the acid was neutralized and the solvent power thereby largely destroyed. The quantity of phosphoric acid dissolved increased with an increase in the quantity of free humic acid present. The numerical agreement, however, was affected by the reabsorption of the phosphoric acid made soluble.

Snyder⁴ prepared humus by mixing soil with such substances as clover, flour, straw, saw dust, and sugar, and allowing to ferment for a year. At the end of that time the humus produced contained more phosphoric acid than was originally present in the humus-forming material, indicating that some of the phosphoric acid of the soil had united with the humus. By "humus"

1 Bied. Centr., 1883, 155.

2 Ann. Chim. Phys., 27, 196.

3 Landw. Jahrb., 1898, IV, 392.

4 Minn. Agr. Expt. Sta. Bull., No. 53.

is here meant the soluble organic matter extracted with a 2 per cent solution of ammonia, after treating the soil with a dilute solution of hydrochloric acid. The "humic phosphoric acid" is the phosphoric acid present in the extractive material. Humic phosphoric acid proved to be one of the most valuable forms.

Dumont¹ investigated the absorbing power of several organic soils containing humus and lime. Mono-calcium phosphate was applied in aqueous solution before and after calcination of the soil. Calcination seemed to decrease the immediate, but increased the final absorption of phosphoric acid. These results were construed as proving the combination of humus with phosphoric acid. The quantities of lime present appeared to have same effect on the absorption, but the relationship of lime, humus, and phosphoric acid was not well defined. Mono-calcium phosphate was also applied to precipitated humus. Absorption took place in the ratio of humus 10, to P_2O_5 1. Precipitated humus was not defined.

The use of ferrous sulphate in agriculture, has not been the object of much experimental enquiry. Griffiths², however, obtained some very interesting practical results by its use, and his work is taken up here because of its bearing on the behavior of phosphoric acid in the soil.

The material was applied at the rate of 50 lbs. per acre. Among the crops grown were hay, mangels, beans, potatoes, and wheat. Applied with farmyard manure, its action was injurious, the poisonous effect being due to the formation of ferrous sulphide. The crops in nearly all other cases were increased largely and the percentage content in phosphoric acid was increased in all cases. The ferrous sulphate was not oxidized rapidly in the soil, its presence being proven six weeks after application. Ferrous sulphate was used in conjunction with superphosphate in all tests.

The subject was taken up a little later by Delacharlony and Destremx³. They found that the sulphate was productive of increased yields only when the soil contained small quantities of iron, the increase ceasing when the ferric oxide reached 3 per

¹ Compt. rend., 1901, **132**, 435.

² Jour. Chem. Soc., Trans. 1884, 71,—1886, 114,—1887, 215.

³ Bied. Centr., 1889, 9.

cent, and was detrimental when 4 per cent was reached. The increase varied with different crops, from 5 per cent to 139 per cent.

Cazeneuve and Nicolle¹ studied the solvent action of ferrous sulphate on some of the phosphatic fertilizers in common use, namely, slag, mineral phosphate, bones, superphosphate, and di-calcium phosphate. After eight days the first three had suffered no change in the amount of phosphoric acid soluble in acetic acid and ammonium citrate. With superphosphate half of the water soluble had become reverted. With the di-calcium phosphate, the phosphoric acid soluble in acetic acid and ammonium citrate had increased, but the change was not to the water soluble form.

The action of ferrous sulphate on crops was investigated by Boiret and Paturel². Seedlings of peas and oats were used in water culture experiments. Even with very dilute solutions, the plants were poisoned, owing to the formation of free sulphuric acid. Iron citrate and citric acid had the same effect. Tests were then made with soils containing known quantities of lime. The sulphate was injurious except when there was present a sufficient amount of lime to neutralize the free acid formed. Analysis of the crops showed that ferrous sulphate had no effect on the amount of phosphoric acid in the product. In these experiments the sulphate was not used in conjunction with other fertilizers, as in the work of Griffiths already quoted.

¹ Chem. Centr., IV, (2) 1892, 121.

² Ann. Agron., 18, 418.

SUMMARY

So far as the writer has been able to ascertain, the literature cited above includes practically all the work relating directly to the subject under investigation. Briefly stated, the following conclusions have been drawn from the work referred to :

I. When soluble phosphates are added to soils the phosphoric acid is usually changed to insoluble forms. The action in most cases is due to chemical change, by virtue of the presence of compounds of iron, aluminum, and calcium, and possibly magnesium. These compounds are easily decomposable salts which can be extracted with hydrochloric acid.

II. Hydrated oxides of iron and aluminum, and carbonate of calcium unite with phosphoric acid very rapidly. The phosphates of iron and aluminum formed are from two to five times as insoluble in pure water as calcium phosphate. They are also less soluble in water containing carbon dioxide and various alkali salts.

III. It is the tendency of phosphoric acid to form the more difficulty soluble compounds in the soil, but not all the phosphoric acid appears to be so combined, nor is such combination always effected with great rapidity. The complete fixation in some cases does not take place for several months.

IV. Mixed with calcium carbonate, in the presence of soil water, phosphates of iron and aluminum undergo decomposition with the formation of calcium phosphate. With certain soils, calcium hydroxide also apparently has a solvent action on the phosphates of iron. Conditions affecting the equilibrium between these compounds have not been determined.

V. Absorption may be influenced to some extent by the presence of some of the alkali salts. The effect is not very well defined. In some cases the solubility of the soil phosphoric acid seems to be increased in the presence of these salts.

VI. In some cases the humus in soils has the effect of rendering insoluble phosphates more available to plants. The action

seems to be due to free humic acid, rather than to salts of this acid. This point, however, has not been determined.

VII. Humus is believed to possess great absorptive properties though experimental evidence supporting this view is exceedingly limited and not very conclusive. The relation between humus and phosphoric acid is not well defined.

VIII. Ferrous sulphate in conjunction with phosphates, applied to some soils is beneficial to crops. It seems to increase the availability of the phosphoric acid. In large quantities on acid soils, it acts as a poison to plants. The injurious effect is due in part to the formation of sulphuric acid. The same effect may be produced in neutral soils, and soils not sufficiently basic to neutralize all the acid formed.

IX. Sand and orthoclase offer no resistance to the extraction of soluble phosphoric acid by pure water.

EXPERIMENTAL

1. *Methods of Determining Phosphoric Acid.*

The work about to be described necessitated a number of phosphoric acid determinations. Hence it was thought advisable in most cases to employ the Optional Volumetric Method of the Association of Official Agricultural Chemists¹. In order to test its accuracy, this method was compared with the Official Gravimetric Method², on a variety of materials typical of those to be considered in the experiments following. The methods were carried out as follows :

Volumetric Method. The sample was dissolved in from 15 to 30 c.c. of strong hydrochloric acid and from 3 to 10 c.c. of nitric acid. The solution was cooled, diluted to 250 c.c., and an aliquot part taken for the determination. This portion was treated with 10 c.c. of nitric acid, nearly neutralized with ammonia, diluted to about 100 c.c., and heated in the water bath to 65 degrees C. Molybdic solution was then added (the amount depending on the amount of P_2O_5 present) the mixture stirred, allowed to stand thirty minutes, and filtered on an asbestos filter. After thorough washing with cold water, the yellow precipitate was returned to the precipitating beaker, dissolved in standard potassium hydroxide, a few drops of phenolphthalein added, and the excess of alkali titrated with standard nitric acid. Each cubic centimeter of the standard potassium hydroxide was equivalent to 1 mg. P_2O_5 .

Gravimetric Method. The sample was dissolved in from 15 to 30 c.c. of strong hydrochloric acid and from 3 to 10 c.c. of nitric acid. The solution was cooled diluted to 250 c.c., and an aliquot part corresponding to 0.3 gram taken for analysis. The solution was treated with 10 c.c. of nitric acid, nearly neutralized with ammonia, diluted to about 100 c.c., and heated to 65 degrees

¹ U. S. Dept. Agr., Div. Chem., Bul. No. 46, 13 (revised).

² Ibid., 10.

C in a water bath. Molybdc solution was then added, the whole digested for one hour at 65 degrees C, filtered and washed thoroughly with cold water. The precipitate was dissolved on the filter with ammonia and hot water, and washed into a beaker to a bulk of not more than 100 c.c. The solution was nearly neutralized with hydrochloric acid, cooled, and magnesia mixture added, drop by drop, from a burette, stirring vigorously. After fifteen minutes, 30 c.c. of ammonia (0.96 sp. gr.) were added, and the whole allowed to stand over night. The precipitate was then collected on a filter, washed with 2.5 per cent ammonia until free from chlorides, dried, ignited to whiteness and weighed. The quantity of P_2O_5 was calculated from the weight of the $Mg_2P_2O_7$, using the factor 0.6396. The following results were obtained.

Material	Grams P_2O_5	
	Gravimetric	Volumetric
"Insoluble" from Superphosphate.....	0.0145	0.0147
"Insoluble" from Superphosphate.....	0.0146	0.0147
Ferric Phosphate.....	0.1146	0.1137
Ferric Phosphate.....	0.1149	0.1140
Aluminum Phosphate.....	0.1137	0.1143
Aluminum Phosphate.....	0.1138	0.1146
Calcium Phosphate.....	0.1361	0.1369
Calcium Phosphate.....	0.1367	0.1374

The results by the two methods agree closely, the difference being within the experimental error usually allowed for such determinations. With the larger quantities of phosphoric acid, the gravimetric method was used as a check on the volumetric. The results in all cases, therefore, are strictly comparable.

II. *Relation Between Phosphoric Acid, and Compounds of Iron, and Calcium.*

Recent results obtained by the use of lime in conjunction with phosphates of various kinds, have suggested new possibilities with regard to the relation between phosphates of iron and calcium in the soil. Lime has hitherto been regarded, partly as a direct plant food, partly as an amendment in liberating plant food, especially potash, but principally as an agent for improving

the physical condition of soils. With regard to the action of phosphoric acid in the presence of calcium (lime and calcium carbonate) and iron, the literature is somewhat contradictory. The reaction to some extent appears to be a reversible one. The mass law, which of late years has served to clear up many unexplained phenomena, undoubtedly plays a very important part.

It occurred to the author that the beneficial effect of lime might be due, to some extent, to the chemical action of this substance in rendering phosphates more available to crops, and that the behavior of phosphoric acid in the presence of compounds of calcium and iron, might depend on the relative quantities of the last two present. The experiments designed to study these points are described under the following heads:

- (a) Action of lime on ferric phosphate.
- (b) " " " " the phosphate formed by fixation.
- (c) " " " " soils.
- (d) Fixation of phosphoric acid in the presence of compounds of iron and calcium.

(a) ACTION OF LIME ON FERRIC PHOSPHATE.

The object of the experiment was to determine the effect of lime on the availability of precipitated and natural ferric phosphates.

The solvent selected for this purpose was the 1 per cent citric acid solution proposed by Dyer¹, for the determination of available plant food in soils. This reagent is the only one of the many solvents proposed for determining available plant food, that has received any favor among agricultural chemists. While it is still of doubtful efficiency in determining absolute availability, in determining relative values, for which purpose it was used in the present work, it has been of unquestioned service. Dyer proposed this reagent as representing the average root juice acidity of a large number of agricultural plants examined by him.

Precipitated ferric phosphate was prepared by treating ferric chloride with di-sodium phosphate. The resulting precipitate was washed thoroughly with cold water and the product air

¹ Jour. Chem. Soc. Trans., 1894, 115.

dried. Phosphoric acid was determined by the gravimetric method, and ferric oxide by the volumetric bi-chromate method. The following results were obtained :

Fe ₂ O ₃	41.53%
P ₂ O ₅	38.20%
H ₂ O	20.08%

Correcting for hygroscopic moisture, the figures agree with the formula FePO₄.2H₂O.

The only natural ferric phosphate that could be obtained was a sample of Dufrenite containing 16.01 per cent of P₂O₅. This is a basic ferric phosphate.

The solubility of these materials was first determined by placing 1 gram in a small flask, adding 100 c.c. of 1 per cent citric acid solution, and allowing to stand twenty-four hours at room temperature, shaking once each hour. The insoluble residue was then filtered off, washed with cold water, and the phosphoric acid determined. The following results were obtained :

Material.	P ₂ O ₅ sol. in 1 per cent citric acid.	Per cent of total.
Precipitated Ferric Phos.	12.20%	31.9
Precipitated Ferric Phos.	12.05%	31.5
Dufrenite	0.07%	0.4
Dufrenite	0.09%	0.5

The effect of lime on the solubility of these phosphates was then determined. For this purpose 1 gram of each of the materials was placed in a flask, pure slaked lime (free from phosphoric acid) added, and enough water to make a thin paste. After twenty-four hours the contents of the flask were treated with 100 c.c. of 1 per cent citric acid solution and an additional amount of the crystallized acid to neutralize the excess of lime. The solubility in the citric acid was then determined as in the first instance. The following table contains the results.

Material.	Lime.	P ₂ O ₅ sol. in 1 per cent citric acid.	Per cent of total.
Prec. Ferric Phos.-----	1 gram	24.95%	65.3
Prec. Ferric Phos.-----	1 gram	24.90%	65.2
Prec. Ferric Phos.-----	0.5 gram	35.80%	93.7
Prec. Ferric Phos.-----	0.5 gram	35.80%	93.8
Prec. Ferric Phos.-----	0.25 gram	37.00%	96.9
Prec. Ferric Phos.-----	0.25 gram	36.90%	96.6
Dufrenite -----	1 gram	0.45%	2.8
Dufrenite -----	1 gram	0.47%	2.9

The following table shows the comparative solubility of the phosphoric acid (P₂O₅) in 1 per cent citric acid, with and without the addition of lime :

Material.	Without lime.		With lime.	
		1 gr.	0.5 gr.	0.25 gr.
Prec. Ferric Phos.--	12.20%	24.95%	35.80%	37.00
Prec. Ferric Phos.--	12.05%	24.90%	35.90%	36.90
Dufrenite -----	0.07%	0.45%	-----	----
Dufrenite -----	0.09%	0.47%	-----	----

It is seen from the above tables that the action of lime on the natural ferric phosphate was not very marked. In the case of the precipitated ferric phosphate the lime caused a considerable increase in the solubility. The larger quantities did not cause as great an increase as the smaller quantities. This fact indicated the formation of the more soluble calcium phosphates with the smaller quantities. With an excess of lime, as in the experiment in which 1 gram was used, tri-calcium phosphate was probably formed, and this compound is much less soluble in 1 per cent citric acid than the di- and mono-calcium compounds.

It is to be remarked that the reaction was fairly rapid. Within one hour after the addition of lime, a red compound began to separate. This compound was probably ferric hydroxide. An attempt was made to separate the products formed in the reaction. Various solvents were tried, but it was found impossible to effect a separation of calcium and ferric phosphates in the presence of ferric hydroxide. In the course of these trials a 5 per cent solution of neutral potassium oxalate was observed to act on precipitated ferric phosphate, dissolving both the iron and the phos-

phoric acid in the proportion in which they existed in the original compound. This action of potassium oxalate was made the basis of a qualitative test for the presence of ferric phosphate, in the presence of ferric hydroxide. The solution was found to have no solvent action on ferric hydroxide. The compound formed with ferric phosphate appeared to be a double oxalate, very soluble in water.

Ferric phosphate was treated with varying quantities of lime. The products of the reaction were treated with the solution of potassium oxalate, filtered, and the filtrate tested for iron. The absence of iron in the oxalate solution was taken as showing the absence of ferric phosphate in the mixture treated with this solvent. 0.2 gram lime was found to be the smallest amount capable of completely converting 1 gram of ferric phosphate.

The behavior of potassium oxalate suggested the use of this reagent for determining the available phosphoric acid in phosphatic materials. A few preliminary trials on its solvent action on calcium and iron phosphates, under different conditions, were made. The results were not sufficiently satisfactory to indicate the usefulness of this reagent.

(b) ACTION OF LIME ON THE PHOSPHATE FORMED BY FIXATION.

It is fairly well established that soluble phosphates when applied to soils tend to pass into comparatively insoluble forms. This reversion is caused largely by hydrated oxide of iron. It was considered important therefore, to know the effect of lime on the compound thus formed.

To this end two grams of pure ferric hydroxide were treated in a small flask with 50 c.c. of an aqueous solution of superphosphate, shaken, and allowed to stand ten days with occasional agitation. The insoluble residue was then filtered off and washed with cold water until phosphoric acid ceased to be given up. The filtrate and washings were then analyzed and the phosphoric acid absorbed calculated. Several residues were obtained in this way. Two of these were treated with 100 c.c. of 1 per cent citric acid solution, and the solubility determined as de-

scribed under ferric phosphate. Four others were treated with 0.5 gram of lime, enough water added to make a thin paste, and the mixture allowed to stand one and nine days. The solubility in 1 per cent citric acid was determined, sufficient crystallized citric acid being added to correct the basicity due to lime. The superphosphate solution originally added contained 0.1340 gram of P_2O_5 . Under "residues" in the following table are included the amounts of P_2O_5 absorbed :

P_2O_5 in residues.	Lime added.	P_2O_5 sol. in 1 per cent citric acid.	Per Cent soluble.
0.1249 grs.	-----	0.0214 grs.	17.1
0.1248 grs.	-----	0.0224 grs.	17.9
0.1244 grs.	0.5 grs. one day	0.0544 grs.	43.7
0.1240 grs.	0.5 grs. one day	0.0535 grs.	43.0
0.1244 grs.	0.5 grs. nine days	0.0499 grs.	40.1
0.1244 grs.	0.5 grs. nine days	0.0495 grs.	39.7

Incidentally a similar experiment was made using neutral ammonium citrate solution (1.09 sp.gr.) as the solvent. For various reasons this solvent was not used in the soil investigations. The preceding plan was followed except that the action of lime was allowed to continue for two days. The results were as follows :

P_2O_5 in residues.	Lime added.	P_2O_5 sol. in am. citrate.	Per Cent soluble.
0.1217 grs.	-----	0.0535 grs.	43.9
0.1211 grs.	-----	0.0534 grs.	44.0
0.1223 grs.	0.5 grs. two days	0.0536 grs.	43.8
0.1224 grs.	0.5 grs. two days	0.0527 grs.	43.0

The results show that lime materially increased the solubility of reverted phosphate of iron in 1 per cent citric acid. The action appeared to be complete in one day. The solubility of the reverted phosphate in ammonium citrate solution was not increased by the addition of lime.

The composition of this phosphate of iron has not been determined. It is much more insoluble in 1 per cent citric acid, and ammonium citrate than the normal ferric phosphate. That none of the latter compound was formed in the fixation experiment, was indicated by the following tests :

(1). Ferric hydroxide and a solution containing phosphoric acid in large excess of the amount necessary to form the normal salt, were allowed to react for weeks. The amount of phosphoric acid absorbed was then determined.

Fe(OH) ₃ used	0.2500 grs.
P ₂ O ₅ absorbed	0.0275 "
P ₂ O ₅ required to form FePO ₄	0.1664 "

Even in the presence of a large excess of phosphoric acid, the ferric hydroxide absorbed little more than one tenth of the amount necessary to form the normal salt.

(2). The compound formed was treated with the 5 per cent solution of potassium oxalate already described. After filtering the filtrate was tested for iron, the absence of which showed the absence of normal ferric orthophosphate.

The compound formed by fixation is evidently a highly basic phosphate of iron. The compound appears to be formed even when only a limited amount of the base is present. In the soil, the bases would usually be present in large excess with respect to the phosphoric acid.

In the experiments just described, the lime was brought into intimate contact with the phosphate of iron. Its action therefore was probably at a maximum. It was thought advisable to supplement this with artificial soil experiments under conditions which usually obtain in soils, conditions presumably less favorable to the action of lime.

For this purpose 200 gram portions of clean sand were extracted with hydrochloric acid and washed free from acid with cold water. A blank experiment showed that the product possessed no absorptive properties for phosphoric acid. Each portion was mixed with 4 grams of ferric hydroxide and placed in a six inch cylinder. Superphosphate solution was then added and absorption allowed to continue for ten days. During the meantime the mixture was kept moderately moist. After ten days the phosphoric acid unabsorbed was washed out with cold water and determined, the amount absorbed being calculated from the data thus obtained. The mixture then represented a soil containing 1.5 per cent Fe₂O₃, and 0.12 per cent of P₂O₅.

For this work and the soil investigation to be described later two solvents were selected, namely, 1 per cent citric acid solution, and $\frac{n}{200}$ hydrochloric acid. The first has already been referred to, but for soil work the conditions attending its use were modified somewhat.

Hydrochloric acid $\frac{n}{200}$ was recently proposed by Moore¹ for the determination of available mineral plant food in soils. In the work referred to pot experiments were made with a large variety of soils, and the amounts of phosphoric acid extracted by the solvent in question agreed closely in nearly all cases with the actual amount removed by the crops.

The solubility determinations with the reagents selected were carried out in the following manner. The ratio of solvent to substance was 500 c.c. to 100 grams. These were placed in a litre glass stoppered bottle, and kept at a temperature of 40 degrees C in a water bath for exactly five hours. The bottles were shaken every fifteen minutes. After the digestion the whole was shaken and emptied on to a folded filter sufficiently large to hold the entire contents of the bottle. After draining, 400 c.c. of the filtrate representing 80 grams of the soil, were evaporated to dryness. In the case of the citric acid the residue was treated with magnesium nitrate solution, evaporated to dryness, and ignited until all organic matter was destroyed. These residues were taken up with water and nitric acid and the phosphoric acid determined.

In all the experiments a preliminary digestion was made with 20 grams of soil and 100 c.c. of the solvent, in order to determine the basicity of the soil. A correction was then made in the strength of the acids so as to reduce the solvent action to a uniform basis.

Portions of the artificial soil described were air-dried and the solubility of the phosphoric acid determined. Lime (one and two grams) was mixed with other portions and the action allowed to go on for seven days, the mixture being kept moist during the meantime. These mixtures were then air-dried and solubility determinations made. The following results were obtained.

¹ Jour. Am. Chem. Soc., 1902, 79.

SOLVENT—I PER CENT CITRIC ACID SOLUTION

P ₂ O ₅ in residues.	Lime added.	P ₂ O ₅ sol. in 1 per cent citric acid.	Per cent soluble.
0.2530 grs.	-----	0.0622 grs.	24.5
0.2540 grs.	-----	0.0611 grs.	24.0
0.2488 grs.	1 gram-----	0.1060 grs.	42.6
0.2483 grs.	1 gram-----	0.1070 grs.	43.0
0.2527 grs.	2 grams-----	0.1232 grs.	48.7
0.2517 grs.	2 grams-----	0.1220 grs.	48.4

SOLVENT—HYDROCHLORIC ACID $\frac{n}{200}$

P ₂ O ₅ in residue.	Lime added.	P ₂ O ₅ sol. in 1 per cent citric acid.	Per Cent soluble.
0.2530 grs.	-----	0.0033 grs.	1.3
0.2540 grs.	-----	0.0038 grs.	1.4
0.2488 grs.	1 gram-----	0.0044 grs.	1.7
0.2483 grs.	1 gram-----	0.0052 grs.	2.0
0.2527 grs.	2 grams-----	0.0048 grs.	1.8
0.2517 grs.	2 grams-----	0.0052 grs.	2.0

From the results it is seen that lime increased the solubility in 1 per cent citric acid considerably as in the preceding experiments. The increase is somewhat less, however, with the artificial soil.

With regard to the solubility in $\frac{n}{200}$ hydrochloric acid, the addition of lime produced little change. The differences are within the range of experimental error. It is to be remarked that the solvent action of the hydrochloric acid was very small.

(c) ACTION OF LIME ON SOILS.

For the purpose of studying the effect of lime on the phosphoric acid originally present in soils, two samples of the latter were taken. The soil designated "A" was a sandy loam under cultivation. Soil "B" was a clay loam not under cultivation.

Samples were prepared for analysis according to the methods of the Association of Official Agricultural Chemists¹.

¹ U. S. Dept. Agr., Div. Chem., Bul. No. 46, 71.

The determination of total phosphoric acid was made, the method being to weigh out 2 grams of soil into a platinum dish and ignite to drive off organic matter. Put in 1 or 2 c.c. of hydrofluoric acid and allow the soil to come in contact with the acid slowly to avoid loss by sputtering. After the violent action has ceased, place on a water bath and evaporate to dryness. After repeating this operation once or twice, take up with a little nitric acid and water and determine phosphoric acid. This method was rapid and gave closely agreeing results. In this way the following results were obtained :

	Soil "A."	Soil "B."
Total P_2O_5 -----	0.145%	0.155%

Complete analyses of the acid soluble materials in these were then made according to the methods of the Association of Official Agricultural Chemists¹, with the following results :

DIGESTION IN HYDROCHLORIC ACID 1.115 SP. GR.

Constituent.	Soil "A."	Soil "B."
Insoluble matter -----	87.85%	83.53%
Potash (K_2O) -----	0.74%	0.80%
Soda (Na_2O) -----	0.20%	0.41%
Lime (CaO) -----	0.11%	0.14%
Magnesia (MgO) -----	0.55%	0.78%
Oxide of Manganese (MnO) -----	0.03%	0.02%
Ferric Oxide (Fe_2O_3) -----	1.74%	1.91%
Alumina (Al_2O_3) -----	4.00%	5.72%
Phosphoric Acid (P_2O_5) -----	0.12%	0.10%
Sulphuric Acid (SO_3) -----	0.04%	0.06%
Carbonic Acid (CO_2) -----	0.26%	0.18%
Volatile matter -----	4.17%	6.51%

Portions of 200 grams of the air dried soils were then mixed thoroughly with lime (one and two grams), the whole placed in cylinders, moistened and allowed to stand exposed to the atmosphere for seven days. The portions were then again air dried, and weighed. The solubility of the original and limed portions in 1 per cent citric, and $\frac{11}{200}$ hydrochloric acids was then deter-

¹ U. S. Dept. Agr. Div. Chem., Bul. No. 46, 72.

mined according to the method described under artificial soils, the quantities taken being calculated on a basis of the original air dry soil. The quantities of phosphoric acid in the following tables are calculated to this basis, and are therefore comparable in all cases.

SOIL "A." SOLVENT—I PER CENT CITRIC ACID

Lime added.	P ₂ O ₅ soluble.	Per cent of total.
None	0.028%	19.3
None	0.030%	20.7
One gram	0.031%	21.3
One gram	0.032%	22.0
Two grams	0.037%	25.5
Two grams	0.038%	26.2

SOIL "B." SOLVENT—I PER CENT CITRIC ACID

Lime added.	P ₂ O ₅ soluble.	Per cent of total.
None	0.0068%	4.3
None	0.0067%	4.3
One gram	0.0132%	8.5
One gram	0.0130%	8.3
Two grams	0.0100%	6.4
Two grams	0.0102%	6.5

SOIL "A." SOLVENT— $\frac{n}{200}$ HYDROCHLORIC ACID

Lime added.	P ₂ O ₅ soluble.	Per cent of total.
None	0.0030%	2.0
None	0.0030%	2.0
One gram	0.0043%	2.9
One gram	0.0041%	2.8
Two grams	0.0040%	2.8
Two grams	0.0038%	2.7

SOIL "B." SOLVENT— $\frac{n}{200}$ HYDROCHLORIC ACID

The amount of phosphoric acid was too small to be determined. The addition of lime (one and two grams), seemed to produce no effect on the solubility of the phosphoric in this soil.

The two soils used in the experiments described contained practically equal amounts of total phosphoric acid, and phosphoric acid soluble in hydrochloric acid 1.115 sp. gr., while the availability of that in the cultivated soil, as shown by the weak acid solvents, was about five times as great as that in the uncultivated soil. The chemical analyses of the two present no differences that could serve as an explanation of the difference in availability. This difference, therefore, is probably due, partly to the state of cultivation, and partly to the physical characteristics of the soils.

From the results obtained it is doubtful whether $\frac{n}{200}$ hydrochloric acid would prove a suitable solvent for the determination of available plant food in all soils. Comparing the two soils, however, the results with it indicate in a general way the same relative availability of the phosphoric acid as is shown by the solubility in 1 per cent citric acid.

In regard to the action of lime, the solubility in citric acid was increased slightly in both soils. The solubility in hydrochloric acid was not increased in the case of the uncultivated soil. This soil evidently held the phosphoric acid in a very insoluble form.

It is interesting to note the difference in action of lime on natural and artificial soils. A comparison is made in the following table.

SOLUBILITY OF P_2O_5 IN 1 PER CENT CITRIC ACID

	Without lime.	With lime.
Soil "A".....	19.3%	21.3%
Soil "A".....	20.7%	22.0%
Artificial soil.....	17.1%	43.7%
Artificial soil.....	17.9%	43.0%

The figures represent per cent of the total phosphoric acid. It is evident that the natural soil was less susceptible to the action of lime than the artificial product.

(d) FIXATION OF PHOSPHORIC ACID IN THE PRESENCE OF COMPOUNDS OF IRON AND CALCIUM

While the tendency of soluble phosphates, applied to soils, is to pass into the insoluble phosphate of iron, several investi-

gators, notably Deherain, Kostitcheff, and others have observed that calcium carbonate reacts with ferric phosphate forming calcium phosphate, the action taking place even in the presence of an excess of ferric hydroxide. Whether this was the reverted or the normal ferric phosphate was not stated.

It occurred to the author that the presence of a relatively large quantity of calcium compounds might interfere with the formation of reverted phosphate of iron. A short experiment was made in order to ascertain whether the presence of calcium carbonate would influence the fixation of phosphoric acid by ferric hydroxide.

Tri-calcium phosphate was dissolved in water charged with carbon dioxide, and 200 c.c. of the solution containing 0.0176 gram of P_2O_5 were added to 1 gram of ferric hydroxide, with and without varying quantities of calcium carbonate. The action was allowed to continue for ten days, after which the mixtures were filtered. The solubility of the residues in ammonium citrate solution was determined by adding 50 c.c. and allowing to stand twenty-four hours in the cold. This residue was filtered and washed with cold water. The results are contained in the following table:

Material mixed with 0.0176 grs. P_2O_5 .	P_2O_5 insoluble in ammonium citrate.
1 gram $CaCO_3$ -----	0.0018 grs.
1 gram $Fe(OH)_3$ -----	0.0145 grs.
1 gram $Fe(OH)_3$ plus 1 gram $CaCO_3$ -----	0.0152 grs.
1 gram $Fe(OH)_3$ plus 2 grams $CaCO_3$ -----	0.0147 grs.

In the blank determination above practically all the phosphoric acid was extracted by ammonium citrate. The presence of calcium carbonate (one and two grams) apparently had no effect on the solubility of the compound formed by the reversion of phosphoric acid.

III. *Behavior of Phosphoric Acid towards Humus*

That humus possesses the power of absorbing phosphoric acid from solution has not been proven. Organic soils have been known to effect solution of insoluble phosphates in some cases,

while in other cases soils containing a large amount of humus exhibited a strong attraction for phosphoric acid.

In studying the retentive power of humus for phosphoric acid it was thought best to work with the artificial preparation, thereby eliminating the possibility of the interference of any other absorbing material.

To this end humic acid was prepared from sugar according to the method described by Berthelot¹. 600 grams of sugar furnished 100 grams of the air dry material. In one portion the moisture was determined by drying to constant weight at 100 degrees C. Other portions were subjected to combustion analysis. The following analysis is calculated on the basis of dry matter.

Carbon	61.48%
Hydrogen	4.74%
Oxygen	33.78%

The phosphoric acid to be absorbed was applied in the form of an aqueous extract of superphosphate, thus approximating conditions which obtain in actual practice. Portions of 1 gram of the air dry humic acid were placed in a small flask, 50 c.c. of a solution containing 0.1550 gram P_2O_5 and 0.0185 gram calcium added to each, and the mixtures allowed to stand one, four and eight days with occasional shaking. At the end of these periods the insoluble matter was filtered off and washed with cold water until the wash water gave no test for phosphoric acid. The quantities of phosphoric acid and calcium in the filtrate and washings were then determined. Calcium was determined by the volumetric permanganate method. The results are found in the following table.

No.	Duration of contact.	P_2O_5 soluble.	Ca soluble.
1	one day	0.1540 grs.	0.0173 grs.
2	one day	0.1545 grs.	0.0180 grs.
3	four days	0.1535 grs.	0.0185 grs.
4	four days	0.1550 grs.	0.0188 grs.
5	eight days	0.1550 grs.	0.0180 grs.
6	eight days	0.1550 grs.	0.0177 grs.

As is shown by the above results, neither the phosphoric acid nor the calcium were retained by the insoluble humic acid.

¹ Chim. Veg. Agr., 4, 123.

It was not expected that chemical absorption would take place. The experiment was suggested by the statements of many writers to the effect that humus is active in retaining plant food by virtue of its physical structure. The data given above indicate that insoluble free humic acid exerts no influence in rendering phosphoric acid insoluble in water.

The organic acids present in the soil do not, however, exist to any great extent in the free state except in bogs and morasses. Soils suitable for agricultural purposes contain little or no free acid except carbonic acid. In most cases they give an alkaline reaction. Humic acid exists as humates of the bases predominating in the soil. These compounds may be divided into two classes, namely, (1) those insoluble or but slightly affected by water, including humates of calcium, magnesium, iron, and aluminum, and (2) those soluble in water including humates of the alkalis. Representative of the first class, calcium humate was selected for study.

This compound was prepared by mixing 10 grams of the humic acid already described with one litre of lime water containing 2.42 grams of CaO , and allowing the mixture to stand for five days with occasional shaking. The insoluble residue was then filtered off and washed with cold water until the washings were neutral. On being subjected to combustion analysis the product showed the following composition, calculated on the basis of dry matter.

Carbon	55.48%
Hydrogen	4.11%
Oxygen	34.81%
Calcium	5.60%

This preparation was treated with a solution of superphosphate in the manner already described for humic acid. The solution contained,

P_2O_5	0.1550 grs.
Ca	0.0185 grs.

The quantities of phosphoric acid remaining unabsorbed by 1 gram of the calcium humate are given below.

Duration of contact.	P ₂ O ₅ soluble.	Ca soluble.	P ₂ O ₅ absorbed.
One day -----	0.1385 grs.	0.0309 grs.	0.0165 grs.
One day -----	0.1385 grs.	0.0312 grs.	0.0165 grs.
Four days -----	0.1360 grs.	0.0278 grs.	0.0190 grs.
Four days -----	0.1365 grs.	0.0283 grs.	0.0185 grs.
Eight days -----	0.1340 grs.	0.0259 grs.	0.0210 grs.
Eight days -----	0.1345 grs.	0.0260 grs.	0.0205 grs.

The above figures show that absorption of phosphoric acid took place to a limited extent. It occurred to the author that a small amount of calcium carbonate might have been formed in the preparation of the calcium humate, in which case the absorption could not be ascribed to the latter compound. Carbon dioxide was determined in a portion of the preparation therefore, the amount obtained being 0.64 per cent. Calculated to calcium carbonate the one gram of the material contained 0.0142 gram of the material contained 0.0142 gram of the carbonate, which in turn would be sufficient to react with 0.0207 gram of P₂O₅ forming the mono-calcium salt. This salt is decomposed by water with the formation of the di-calcium phosphate which is not soluble in water. The absorption therefore is to be referred to the presence of calcium carbonate.

The increase of the calcium in solution was due to the formation of some of the mono-calcium phosphate from the free phosphoric acid present in the superphosphate solution.

It is to be inferred from these facts that calcium humate does not take part in the absorption of phosphoric acid from superphosphate.

As the majority of the humus compounds found in the soil contain nitrogen, it was thought advisable to include some of these in the present work. The compounds used were soluble and insoluble ammonium humate.

For the preparation of these 25 grams of humic acid were treated with 500 c.c. or ammonia solution containing 14.3 grams of ammonia, the flask closed, shaken and allowed to stand five days. The insoluble residue was then filtered off and washed until free from ammonia. When dried the product weighed 11 grams showing that a little more than half of the humic acid had been dissolved by the ammonia. The soluble portion was put

into an evaporator and allowed to stand in the cold until all free ammonia had evaporated. The solution was reserved for further investigation.

The insoluble portion was subjected to a combustion analysis. The "nitrogen as ammonia" represents the amount of nitrogen expelled by boiling with magnesia.

Carbon	62.29%
Hydrogen	5.62%
Oxygen	28.81%
Nitrogen (total)	3.28%
Nitrogen (as ammonia)	1.08%

Although humus varies in its content of nitrogen (depending on the material from which it is formed) the above agrees fairly well with the average analysis of humus extracted from soil by various solvents. Regarding the form in which nitrogen is held in this compound, Berthelot has shown that besides ammonia, it is present most probably as amide. This fact is in accordance with the data obtained when working with the natural product.

The action of this substance on superphosphate was investigated. The material was treated with a solution of superphosphate in the manner already described for humic acid. The solution contained,

P_2O_5	0.1550 grs.
Ca	0.0185 grs.

The quantities of phosphoric acid remaining unabsorbed by 1 gram of the insoluble ammonium humate are given below.

No.	Duration of contact.	P_2O_5 soluble.	Ca soluble.
1	one day	0.1540 grs.	0.0185 grs.
2	one day	0.1545 grs.	0.0178 grs.
3	four days	0.1540 grs.	0.0191 grs.
4	four days	0.1540 grs.	0.0183 grs.
5	eight days	0.1540 grs.	0.0178 grs.
6	eight days	0.1540 grs.	0.0187 grs.

The results show that the insoluble ammonium humate exerted no influence in retaining the phosphoric acid of superphosphate. The content in calcium was also not affected.

The soluble ammonium humate already referred to contained,

Nitrogen (total)	20.25%
Nitrogen (as ammonia)	9.65%

calculated on a basis of dry matter. With a solution of superphosphate, this substance produced a brown flocculent precipitate. Thinking that this precipitate consisted of calcium humate, another portion of the ammonium humate solution was treated with lime water. No precipitate was formed. Neither calcium chloride or ferric chloride produced any change. On adding pure orthophosphoric acid a brown precipitate was formed apparently identical with that formed with the superphosphate solution. These facts indicated the formation of an organic compound containing phosphoric acid. An attempt was made to separate this compound, but it was exceedingly difficult to wash, and apparently underwent partial decomposition.

From the foregoing data it appears that insoluble humus offers no resistance to the extraction of the phosphoric acid of superphosphate by water. The soluble humus appears on the other hand to form an insoluble compound with phosphoric acid, and thus acts as an absorbent. To what extent such absorption may take place was not determined.

(b) SOLUTION

The solvent action of two of these humus compounds was considered briefly. For this purpose precipitated tri-calcium phosphate, humic acid, and soluble ammonium humate were selected. The experiments were carried out as follows.

Portions of 0.5 gram of pure precipitated tri-calcium phosphate were placed in small flasks, and to some of these was added 1 gram of insoluble humic acid, and 10 c.c. of water. To other portions were added 10 c.c. of the solution of ammonium humate. The contents of the flasks were shaken occasionally for five days, after which the residues were filtered off, washed with cold water, and the phosphoric acid determined in the filtrate and washings.

A blank experiment was made with 0.5 gram of precipitated tri-calcium phosphate and 10 c.c. of water treated as described

for the other experiments. The results of these tests are given in the following table.

Material,	P ₂ O ₅ soluble in water.
Tri-calcium phos. 0.5 gr.	none
Tri-calcium phos. 0.5 gr.	none
Tri-calcium phos. 0.5 gr. am. humate 10 c.c. .	none
Tri-calcium phos. 0.5 gr. am. humate 10 c.c. .	none
Tri-calcium phos. 0.5 gr. humic acid 1 gr.	0.0030 gr.
Tri-calcium phos. 0.5 gr. humic acid 1 gr.	0.0028 gr.

The ammonium humate was without action on the tri-calcium phosphate. The free humic acid rendered a portion of the phosphoric acid soluble in water, though the action was not very great. These facts are in accordance with the observations of other workers, namely, that humus is active in rendering insoluble phosphoric acid available to plants. The results presented herewith indicate that this action is due to the humic acid and not to the compounds of humic acid, namely, the humates.

IV. *Absorption of Phosphoric Acid by Zeolites*

There is abundant evidence to show the existence in soils of easily decomposable silicates analogous to the zeolites. The power of these substances to fix the bases potassium, sodium, calcium, ammonia, and magnesium has been thoroughly investigated by a number of workers.

The work of Doelter (1), Friedel (2), Rinne (3), Clarke (4), and others on the constitution and properties of the zeolites, suggested to the writer the possibility of the power of these substances to absorb phosphoric acid.

For this investigation both the artificial and natural silicates were used. The first was prepared by treating a solution of soda alum with a solution of sodium silicate. The resulting precipitate was washed thoroughly with cold water, filtered and dried. The product was difficult to wash, and seemed to undergo partial decomposition even in cold water, with the elimination of sodium silicate. The dry material was found to contain the following:

Alumina	18.12%
Silica	57.21%
Soda	5.85%
Water	18.82%

Two grams of this substance were treated with superphosphate solution, allowed to stand seven days, filtered, washed, and the phosphoric acid in solution then determined. The residues were treated with 100 c.c. of 1 per cent citric acid solution and allowed to stand for twenty-four hours. The phosphoric acid dissolved by this reagent was then determined, with following results :

No.		P ₂ O ₅ absorbed.	Per cent sol. in 1 per cent citric acid,
1	-----	0.1340 grs.	56.8
2	-----	0.1340 grs.	57.4

The natural silicates used were selected with a view of obtaining as much variety in composition as possible. A few insoluble silicates were also used.

It is not within the province of this paper to enter into a discussion of the constitution of these compounds. The empirical formulas are given herewith.

Analcite	NaAlSi ₂ O ₆ · H ₂ O	
Chabazite	(CaNa ₂)Al ₂ Si ₄ O ₁₂	6H ₂ O
Halloysite	H ₄ Al ₂ Si ₂ O ₇ · aq.	
Heulandite	H ₄ CaAl ₂ (SiO ₃) ₆	3H ₂ O
Prehnite	H ₂ Ca ₂ Al ₂ (SiO ₄) ₂	
Pyrophyllite	H ₂ Al ₂ (SiO ₃) ₄	

In order to determine the absorptive power of these substances for phosphoric acid, 2 gram portions of each were placed in small flasks, and to each were added 50 c.c. of a solution of superphosphate containing 0.1550 gram P₂O₅. The experiment was carried out in the manner described for the precipitated silicate. Solubility determinations of the residues, in 1 per cent citric acid were made in a similar way. A check determination was made with washed sand. The following table contains the data obtained.

Material.	P ₂ O ₅ absorbed.	Per cent sol. in 1 per cent citric acid.
Sand	none	----
Analcite	0.0305 grs.	46.5
Analcite	0.0295 grs.	44.7
Chabazite	0.0170 grs.	100.0
Chabazite	0.0165 grs.	100.0
Halloysite	0.0125 grs.	80.8
Halloysite	0.0125 grs.	80.8
Heulandite	0.0130 grs.	100.0
Heulandite	0.0125 grs.	100.0
Prehnite	0.0125 grs.	77.6
Prehnite	0.0120 grs.	76.6
Pyrophyllite	none	----

The results show that some of the natural silicates (zeolites) possess an absorptive power for phosphoric acid, while the artificial preparation did so to a marked degree. The compounds formed appeared to be more soluble in 1 per cent citric acid than the compound formed when ferric hydroxide was the absorbent.

The nature of this absorption is not understood. In the light of our present knowledge of the zeolites present in the soil it was considered impracticable to undertake to ascertain its nature.

It occurred to the writer that this absorption might be due to the presence of free hydrated oxide of aluminum, in which case the action could not properly be referred to the silicates in question. In order to determine this point, some representative samples of the materials used were strongly dehydrated over the blast lamp and the absorptive power again determined with the following results:

Material.	Before dehydration P ₂ O ₅ absorbed.	After dehydration.
Analcite	0.0305 grs.	0.0348 grs.
Analcite	0.0295 grs.	0.0348 grs.
Chabazite	0.0170 grs.	0.0170 grs.
Chabazite	0.0165 grs.	0.0175 grs.
Precipitated silicate.....	0.1340 grs.	0.1170 grs.
Precipitated silicate.....	0.1340 grs.	0.1170 grs.

With analcite dehydration seemed to increase the absorptive power though only to a slight extent. Dehydration of the arti-

ficial preparation decreased slightly the absorptive power, indicating the presence of a small amount of aluminum hydroxide.

It is doubtful whether there exists in soils silicates identical either with the natural or the artificial materials used in the above work. But it is believed that the data here presented serves to show that the zeolitic silicates in soils may take part in the fixation of phosphoric acid.

V. *Action of Ferrous Sulphate*

The value of ferrous sulphate in agriculture appears to be questionable. Regarding its action towards phosphoric acid, two possibilities suggested themselves, namely, (1) the hydrolysis and consequent solvent action of the sulphuric acid formed, on the insoluble phosphates, (2) the action in retaining the phosphoric acid applied in a comparatively soluble form.

The solvent effect on several phosphatic materials was determined by placing 1 gram of each in a flask and treating with 1 gram of ferrous sulphate, 100 c.c. of water, and shaking occasionally for four days. The residues were filtered, washed, and the filtrate tested for phosphoric acid. None was present in any case. The residues were then treated with 100 c.c. of 1 per cent citric acid, and the solubility of the phosphoric acid in this reagent determined. The following table contains the data showing the effect of ferrous sulphate on the solubility in 1 per cent citric acid.

SOLUBILITY IN 1 PER CENT CITRIC ACID

Material.	No FeSO_4 .	FeSO_4
	P_2O_5 dissolved.	P_2O_5 dissolved.
Tri-calcium phosphate	26.40%	20.40%
Tri-calcium phosphate	26.20%	20.50%
Ferric phosphate	12.05%	11.50%
Ferric phosphate	12.20%	11.25%
Apatite	1.47%	1.36%
Apatite	1.47%	1.44%
Wavellite	trace	trace
Wavellite	trace	trace

Ferrous sulphate did not increase the citric acid solubility of the phosphates under investigation. In fact with the tri-calcium the effect was to lessen the solubility.

The remarkable effect of ferrous sulphate when used with superphosphate as was the case in the field tests made by Griffiths, indicated that the substance converted the phosphoric acid into forms more available than the reverted phosphate formed from ferric hydroxide.

The precipitate formed on the addition of superphosphate to ferrous sulphate was found to be easily soluble in 1 per cent citric acid. In order to determine whether this compound is formed in the presence of ferric hydroxide, 2 grams of the latter were mixed with 0.5 gram of ferrous sulphate and 50 c.c. of superphosphate solution. Of the reverted phosphate of iron formed from ferric hydroxide without the sulphate, 17.3 per cent of the phosphoric acid was soluble in 1 per cent citric acid, while the compound formed when ferrous sulphate was present showed 19.0 per cent citric acid solubility.

It is improbable therefore that ferrous sulphate can be of any benefit as a retentive agent for phosphoric acid, especially when there is sufficient ferric hydroxide present.

CONCLUSIONS

Summarizing briefly, the writer thinks that the following conclusions are supported by the foregoing work.

I. Lime increases considerably the solubility of precipitated ferric phosphate in 1 per cent citric acid solution. The nature of the calcium phosphate formed depends on the relative amount of lime added. The reaction takes place with moderate rapidity. The solubility of dufrenite is increased by the addition of lime, though not to a very marked degree.

II. Reverted phosphate of iron, formed when phosphoric acid is absorbed by ferric hydroxide, is not identical with normal ferric phosphate. It is much less soluble in 1 per cent citric acid. The addition of lime to reverted phosphate of lime increases its solubility in 1 per cent citric acid. The solubility in $\frac{11}{200}$ hydrochloric acid is increased only to a slight extent. The solubility in neutral ammonium citrate solution is not increased. Reverted phosphate of iron appears to be a highly basic compound.

III. Lime applied in moderate amounts to the soils used, increased the solubility of the phosphoric acid, in 1 per cent citric acid, though the increase was small. The solubility in $\frac{11}{200}$ hydrochloric acid was affected to a less degree, and in one of the soils used no action occurred. The latter reagent, as a solvent for the available phosphoric acid in soils, is of doubtful utility.

IV. The phosphoric acid originally present in soils is much less susceptible to the action of chemical agents than reverted phosphate of iron. The latter probably becomes more resistant with age.

V. The presence of calcium carbonate in relatively large amounts, appears to have no effect on the solubility, in ammonium citrate, of the compound formed by fixation.

VI. Insoluble humic acid, calcium humate, and insoluble ammonium humate offer no resistance to the extraction of the phosphoric acid of superphosphate by water. Soluble ammonium humate forms with superphosphate solution, an insoluble compound whose composition and properties have not been determined. The absorptive property of humus is due probably to the humus compounds soluble in water.

VII. Soluble ammonium humate does not effect solution of precipitated tri-calcium phosphate. Insoluble humic acid renders a portion of the phosphoric acid soluble in water.

VIII. Some of the zeolites and similar hydrous double silicates are capable of abstracting phosphoric acid from solution. The property is not destroyed by strong ignition. The compounds formed are comparatively soluble in 1 per cent citric acid.

IX. The solubility of tri-calcium phosphate, ferric phosphate, apatite, and wavellite, in water and in 1 per cent citric acid, was not increased by the addition of ferrous sulphate. With tri-calcium phosphate, the solubility in 1 per cent citric acid was decreased, indicating that the application of ferrous sulphate under some circumstances may be detrimental.

X. Ferrous sulphate forms with superphosphate a compound soluble in 1 per cent citric acid. In the presence of ferrous sulphate, and ferric hydroxide, the compound formed with superphosphate, has practically the same solubility in 1 per cent citric acid as the compound formed when ferrous sulphate is absent. The latter possesses therefore no especial value as a retentive agent for phosphoric acid.

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